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PHOTON DEGRADATION EFFECTS IN TERRESTRIAL SOLAR CELLS

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E-9664

ABSTRACT

An unexplained instability in terrestrial solar cell output under various use conditions has been observed. The effect is similar to but not identical with previously observed photon-induced degradation phenomenon in radiation damaged space solar cells. Reduction in cell output is observed in N^+/P cells upon exposure to illumination or upon the application of a sufficiently high forward bias. Conversely, an enhancement in output is observed when P^+/N cells are illuminated. Investigations performed on N^+/P cells indicates that a recombination center located at E_c - 0.37 eV in the forbidden band is responsible for the loss in output. The center is electrically inactive in its ground state but can be activated either by raising the minority carrier quasi-Fermi level sufficiently close to the latent center energy level in the band gap, or by direct excitation of electrons from the valence band to the latent center level. The center has been identified as a complex of a lattice defect and a silver atom or cluster of atoms. The effect can be prevented either by preventing the introduction of silver or by eliminating lattice damage through sufficient surface material removal prior to diffusion while at the same time restricting diffusion temperatures to 875° C or less. The effect in N-base cells is not fully understood at the present. It appears, however, that in either type of cell it is the P material that is responsible for the observed instabilities.

INTRODUCTION

In the course of a DOE sponsored effort at the NASA Lewis Research Center to establish reference conditions and methodology for measurement of terrestrial solar cell performance, an unexplained instability in silicon solar cell output under various use conditions was noted. The effect was observed, albeit to varying degrees, in cells from all manufacturers supplying the DOE/JPL Low Cost Silicon Solar Array Project (1). Upon investigation it became apparent that the effect was related to previously reported photon-induced degradation phenomena (2-4), although several significant differences were found. Because of this similarity, the effect will be referred to herein as the terrestrial photon degradation (TPD) effect.

This report describes the effect and presents an analysis of the data which results in an identification of the mechanisms involved. Based on the insights so gained, several methods of eliminating the effect are suggested.

EXPERIMENTAL OBSERVATIONS

N^+/P Cells

The PD effect is characterized in N^+/P cells and modules by a time dependent reduction in cell output. The reduction is observed after the device is exposed to any one of the following modes of operation:

1. Operation at open circuit under illumination intense enough to produce an open circuit voltage, V_{oc}, greater than approximately 0.5 volts.
2. Operation in the dark under a forward bias greater than about 0.5 volts.
3. Operation at short-circuit under illumination that contains certain appropriate wavelength components.

Figure 1 illustrates the degradation of an N^+/P module exposed to natural sunlight for five minutes while at open circuit. A reduction is observed in the short-circuit current (I_{sc}) and to a lesser extent in the V_{oc}. The fill factor does not seem to be affected. Figure 2 shows the effect of degradation on cell spectral response. The drop in red response correlates with the results of diffusion length measurements where a TPD induced decrease of 30% was observed.

There appears to be a threshold bias voltage necessary to induce degradation. Figure 3 shows the current degradation caused by operating cells of various base resistivity for 45 seconds at each of a number of dark bias voltages. As can be seen from the figure, there is a critical voltage below which the cell is stable and above which degradation occurs. Threshold voltages of 0.57 and 0.52 volts were found for the 1 and 7 ohm-cm cells, respectively.

Similarly, a critical open-circuit voltage is required to initiate degradation when a cell is operated under illumination. For degradation to occur in 7 ohm-cm base resistivity cells, for example, the illumination must be intense enough to produce a V_{oc} of 0.5 volts or greater.

The rate of degradation under short-circuit conditions is considerably lower than that under open-circuit conditions. For the cell shown in fig. 4, a sixty minute exposure to unfiltered tungsten light while at short circuit produces a current drop of about 7%. The same cell, under the same illumination conditions, but operated at open circuit exhibited an 8% decrease in current after being exposed for only 5 minutes.

The rate of degradation under short-circuit conditions can be reduced considerably if the long wavelength component of the illumination is removed. This is illustrated in fig. 4 where the effect of using light filtered through 5 cm of water can be seen. The filter eliminates wavelengths greater than about 1.2 μm. In a similar manner, the I_{sc} - induced degradration rate under xenon illumination is considerably lower than that under red-rich tungsten light.

The TPD effect is reversible in that degraded cells can be restored to their original state by appropriate thermal treatment. Measurement of the isothermal recovery time as a function of cell temperature has yielded a recovery activation energy of 0.7 eV. The same annealing characteristics were found regardless of the degradation mode used.

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P^+/N Cells

The mechanisms operating in N-base devices appear to be more complicated than in P-base devices. Certain of the conditions that produce degradation in the N^+/P cells produce an enhancement in the P^+/N cells. For example, P^+/N cell operation under illumination at open-circuit produces a significant increase in cell output. This increase is manifested as an enhancement in the cell blue response, as illustrated in fig. 5. It was found, further, that in order to produce this enhancement, the illumination source must contain light in the wavelength range $0.35 < \lambda < 0.45$ μm. No enhancement or degradation was found for P^+/N devices operated under dark forward bias.

Although the activation energy for thermal annealing has not been determined for P^+/N devices. The annealing characteristics have been found to be qualitatively similar to those for the N^+/P devices.

DISCUSSION AND ANALYSIS

The following is a description of the mechanisms involved in the TPD effect as determined to date. Except where otherwise state the following discussion is limited to the N^+/P device.

Surface Effects

A number of experiments were performed to establish whether or not surface phenomena are responsible for the observed effects. These included:

1. Removal of anti-reflection coatings
2. Variation of the rear surface recombination velocity
3. Measurement of current-voltage characteristics at low temperatures (78^o) to indicate the possible presence of rectifying rear contacts.

The results indicated that none of these surface effects are involved in the TPD effect.

Localized Bulk Effects

Since surface effects have been ruled out, the TPD effect can be attributed to changes in bulk recombination characteristics, that is, to the activation, via the previously described modes of operation, of otherwise latent recombination centers in the bulk of the cell.

While it is clear that the centers are located in the cell bulk, it is not at all certain that they are uniformly distributed. In fact, as we will attempt to show next, the activated centers appear to be localized in a narrow region of the cell base adajcent to the depletion region.

It can be concluded, first of all, from the spectral response changes attendant to the degradation effect in N^+/P cells (fig. 2), that the responsible recombination centers are located in the base (P) region of the cell and not in the diffused (N^+) region. A further localization is indicated by the fact that the effect can be induced by the application of a dark forward bias. Since only the depletion region and its near environs are affected by the application of a bias, one can conclude that the responsible centers in the base region are localized near the depletion region.

A question arises at this point, however, as to whether such a very localized change in recombination characteristics could cause the observed spectral response changes (fig. 2). A series of calculations was performed therefore, to answer this question. The model used in the calculation consisted of a cell in which the diffusion length in a thin layer of the base, adajcent to the junction, could be varied independently of the diffusion length in the remainder of the base.

Illustrated in fig. 6 is an example of the calculated changes in spectral response that are effected when the diffusion length, L^*, in a 5-μm thick layer adjacent to the depletion region is reduced from the original base region value. The results indicate that changes in diffusion length in a very thin layer near the depletion region can indeed alter spectral response characteristics in a manner similar to that observed in the TPD effect.

The TPD effect appears to be caused, therefore, by the localized activation of latent recombination centers, the activated centers being located in the near vicinity of the depletion region in the cell base.

General Model

The conversion mechanism whereby latent centers are converted to active recombination sites is suggested by the fact that both the open-circuit degradation mode and the dark forward bias degradation mode involve a localized increase in the minority carrier concentration and hence a rise in the minority carrier quasi-Fermi level in the vicinity of the depletion region edge. The model adopted here is based on this common factor (i.e., on the relation between the quasi-Fermi level and the latent center energy level).

It is suggested, specifically, that degradable silicon contains latent recombined centers that are converted to active recombination sites by a change in charge state. This change in charge state is brought about when the minority carrier quasi-Fermi level is brought sufficiently close to the latent center level. The position of the quasi-Fermi level can be controlled either by the application of a dark bias or by operating the cell under illumination (5).

The application of a forward bias causes a rise in the minority carrier quasi-Fermi level at the depletion region edge equal to the product of the applied voltage and the electronic change. It is thus possible to estimate the location of the latent center energy level from a knowledge of the threshold bias for degradation. This is illustrated in fig. 7.

In the case of 7 ohm-cm P-type silicon, the majority carrier Fermi level, E_F, lies at $E_V + 0.23$ eV. According to fig. 3 a threshold bias, V_T, of 0.52 volts is necessary to initiate the degradation process. With the assumption that this bias is sufficient to raise the quasi-Fermi level to the latent center level, one can conclude that the latent level, E_L, lies at $E_c - 0.37$ eV.

This reasoning leads to the same value when we consider 1 ohm-cm cells. In this case the Fermi level is located at $E_V + 0.18$ eV and the measured threshold bias (fig. 3) is 0.57 volts. Again the position of the latent level is calculated to be $E_c - 0.37$ eV.

The model is further strengthened by threshold bias measurements made as a function of temperature. The results of measurements made at -25^o, $+25^o$, and $+75^o$ C on a 7 ohm-cm cell are given in fig. 7. Again, even though the Fermi level varies with temperature, the resultant latent center energy level is found in each case to be in the vicinity of $E_c - 0.37$ eV.

Figure 8 shows the saturation degradation levels for several values of dark forward bias. The extent of degradation is seen to be a direct function of bias. This is again what would be expected according to the proposed model since the volume of the cell in which

the quasi-Fermi level exceeds the latent center level varies directly with the applied voltage.

The situation is altered somewhat when degradation under short-circuit conditions is considered. In this case the change in charge state cannot be attributed to quasi-Fermi level changes. The suggested explanation is that under short-circuit conditions degradation occurs through the direct excitation of electrons from the valence band to the E_C - 0.37 eV level. Since the barrier height for direct excitation to this level is 0.75 eV, a photon wavelength of 1.65 μm would be required. The excitation appears to be energetically specific in that wavelengths below about 1.2 μm (fig. 4) are not effective in causing degradation in the I_{SC} mode. It should be noted, finally, that direct excitation will occur whenever light containing the long wavelength component is incident on the cell, even under V_{OC} conditions.

In summary, it is proposed that degradable silicon contains latent recombination centers that are activated through the induction of a charge state change. The change in charge state can be brought about either by bringing the minority carrier quasi-Fermi level into coincidence with the latent center level or by direct excitation of electrons from the valence band to the latent center level.

The mechanisms operating in the P^+/N cell are not clear at the present. The data (fig. 5) do indicate, however, that the effect is caused by changes in diffused (P^+) region collection efficiency. Thus, as it is in the case of the N^+/P cells, changes in the characteristics of the P material are responsible for the observed TPD effects.

Nature of Recombination Centers

General characteristics. - In an attempt to characterize the centers responsible for degradation, a series of experiments were performed. These involved the fabrication of cells using various initial silicon materials, diffusion processing, and surface treatments. It should be noted that the surface treatments to be described are actually means of creating subsurface lattice damage. It is known, for example, that the lattice disturbance resulting from lapping or sawing a silicon crystal extends considerable distances (5 to 50 μm) into the crystal bulk (6).

The initial materials were (1) silicon obtained from terrestrial cells that exhibited the PD effect, (2) 10 ohm-cm crucible-grown silicon, and (3) 1 ohm-cm float zone silicon. The diffusion processes were (1) $POCl_3$ gaseous diffusion, and (2) diffusion from a spin-on doped oxide. All diffusions were performed at 875° C for 30 minutes. Surface conditions included (1) chemically polished surfaces, and (2) mechanically damaged (saw out or lapped) surfaces. The extent of degradation in cells thus processed is shown in fig. 9 where the experimental matrix is displayed.

The major conclusion to be drawn from fig. 9 is that in order for a cell to exhibit TPD effects, two factors must be present. These are (1) sufficient lattice damage, and (2) an impurity species which is either present in the initial material or introduced during cell processing. Neither of these, by itself, is sufficient to produce the effect.

The lattice damage requirement is evident from fig. 9 where it can be seen that in no case does degradation occur in cells that are chemically polished prior to junction diffusion. On the other hand, not all cells fabricated with damaged surfaces exhibit degradation, indicating that lattice damage, while necessary, is not sufficient to cause degradation. A second component must therefore be involved.

The fact that gaseous-diffused 10 ohm-cm cells are stable while cells made from the same material but diffused from a doped-oxide source are not suggests that the second component is an impurity species introduced during the doped-oxide diffusion process. This lattice damage-impurity complex hypothesis can be shown to be consistent with the remaining data in fig. 9.

The cells fabricated from material taken from degrading terrestrial cells, for instance, show degradation regardless of the diffusion process used. This is to be expected, according to the above reasoning, since the cells from which this material was taken had exhibited TPD effects and the responsible impurity would therefore have been present in the silicon material prior to the cell fabrication described here.

The cells made from 1 ohm-cm material are seen to degrade even though clean gaseous diffusions were employed. Doped-oxide diffusions into the same material, however, consistently produce cells with 4 to 5 times greater degradation. These facts can be explained if we assume that the responsible impurity was present to some extent in the initial material and its concentration was increased significantly during the doped-oxide diffusion. Thus it appears that the evidence in fig. 9 is consistent with a lattice defect-impurity complex mechanism.

Process induced lattice damage. - The data in fig. 9 indicate that TPD effects can be prevented if lattice damage due to mechanical surface deformation is eliminated by proper treatment of the silicon wafer before cell fabrication. In the course of this work, however, an additional source of degradation inducing lattice damage was encountered. It was found that cells diffused above a critical temperature showed degradation effects even though polished silicon wafers were used. As long as the diffusion temperatures were held at 875° C or below, degradation effects were negligible. As the temperature was raised above this value, the magnitude of the degradation was seen to increase proportionality. This is illustrated in fig. 10 where extent of degradation is plotted against diffusion temperature for a number of 30-minute doped-oxide diffusions into 1 ohm-cm float-zone material.

This finding correlates with the results of thermal annealing studies done on strained silicon crystals (7). It was found that a deformed silicon lattice can recover without dislocation formation when annealed below 900° C and with dislocation formation above 900° C. It is known that the introduction of a high concentration of phosphorus atoms into the silicon lattice produces large stresses in the lattice (8). This is due to the fact that there is a sizeable mismatch between the phosphorus and the silicon atomic radii. The relief of these stresses at high temperatures (T > 900° C) with attendant dislocation formation would provide the required lattice damage.

In additional restriction is therefore placed on the production of stable solar cells. In order to avoid diffusion-induced lattice damage, diffusion temperatures must be held to 875° C or lower as long as the undesirable impurity is present in either the initial silicon material or in the diffusion source.

Identification of the TPD impurity. - The final step in the characterization of the TPD recombination

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center is the identification of the responsible impurity. The accomplishment of this task was greatly facilitated by the knowledge that the TPD impurity is contained in the doped-oxide diffusion source used here. This fact permitted us to determine the diffusion coefficient of the TPD impurity. Once the diffusion coefficient was known, the number of suspected elements was reduced to such an extent that we were able to isolate the harmful species.

The TPD impurity diffusion coefficient was determined as follows. A number of 1 ohm-cm float zone P-type silicon wafers were diffused from the impurity-containing doped-oxide source at 875° C for 30 minutes. After diffusion the diffused faces of the wafers were mechanically lapped to various depths. The lapped faces of the wafers were then rediffused at 875° C for 30 minutes using a clean gaseous source. The wafers were then contacted and the extent of degradation of the completed cells under open-circuit conditions was determined. The measured degradation is plotted in fig. 11 as a function of the amount of material removed (lapping depth). As can be seen, the amount of degradation decreases with lapping depth, reaching background levels of 1 to 2% after 100 μm has been removed. The concentration of the impurity is evidently low enough at this depth so that TPD effects, if present, are below the limits of detectability. From this 100 μm diffusion depth and a few reasonable assumptions the diffusion coefficient was determined.

The depth of diffusion, x, into a semi-infinite solid from a nondepletable source can be expressed as (9)

$$x = 2\sqrt{Dt}\ \mathrm{erfc}^{-1}\ (C_B/C_O)$$

where D is the diffusion coefficient, t is the time of diffusion, and C_O and C_B here are the diffusant surface concentration and the concentration for which the TPD effect ceases to be measurable, respectively. A determination of D from this equation requires a knowledge of the ratio C_B/C_O. We do not, at this point, however, have any information on the values of C_B or C_O. The best we can do, therefore, is to set wide limits in an attempt to bracket the range of interest. By assuming for instance, that $10^{-10} < C_B/C_O < 10^{-2}$, and remembering that the total diffusion time was 60 minutes, we find that, at 875° C, D lies somewhere between 3×10^{-10} and 1×10^{-9} cm^2/sec. This would place the TPD impurity intermediate between the fast diffusers, such as iron, and the slow diffusers, such as phosphorus, in a group consisting of silver, sulfur, nickel, and gold (10).

The next step consisted of the fabrication and testing of cells that contained appreciable quantities of silver, sulfur, nickel, and gold. Thus 1 ohm-cm P-type float zone wafers with the required lattice damage (saw cut or lapped surfaces) were diffused first with suspected impurity and then with phosphorus in a clean gaseous system. The silver, nickel, and gold diffusions were made from an evaporated metal layer, while the sulfur diffusions were made from a sulfur doped glass.

The cells thus fabricated were tested for the TPD effect. While the sulfur-, gold-, and nickel-doped cells indicated only background levels of degradation, the silver doped cells were highly unstable. Repeated fabrication of silver-doped cells using various initial materials and silver sources has substantiated the initial findings. An analysis of the doped oxide diffusion source has, furthermore, confirmed the presence of silver.

It can be concluded, therefore, that the cause of the TPD effect is a recombination center which is comprised of a lattice defect and a silver atom or complex of atoms.

It should be noted in connection with these results that a heretofore unsuspected source of silver contamination and thus degradation may be the cell contact metallization. At normal sintering conditions of 550° C for 20 minutes silver present in the contacts can diffuse to a depth of several micrometers. Thus it is possible that this source is at least partially responsible for the photon degradation effects observed not only in terrestrial cells but also in space cells after electron and proton irradiation.

CONCLUSIONS

The major conclusions to be drawn from the preceding analysis on P-base solar cells are:

1. The photon degradation effect is caused by a recombination center, the formation of which requires the simultaneous presence of a lattice defect and a silver atom or complex of atoms.
2. The center is electrically inactive in its equilibrium state. The energy level of the inactive center is located in the band gap, 0.37 eV below the conduction band.
3. Conversion to an active recombination center can be brought about either by raising the minority carrier quasi-Fermi level to coincide with the position of the latent center level in the band gap, or by the direct excitation of electrons from the valence band to the latent center level.
4. The recombination center is metastable in its active state, requiring thermal activation to return to its ground (inactive) state. Thermal recovery is characterized by an activation energy of 0.7 eV.
5. Photon degradation can be prevented either (a) by preventing the introduction of silver through the use of a clean diffusion system and clean initial material, or (b) by eliminating lattice damage both through sufficient surface material removal prior to diffusion while at the same time restricting diffusion temperatures to 875° C or below.

Although the effect in N-base devices is not fully understood at the present time, it appears to be due to changes in the recombination characteristics in the diffused (P^+) layer. Thus, in either type cell, it is the P material that is responsible for the observed degradation (enhancement) effects.

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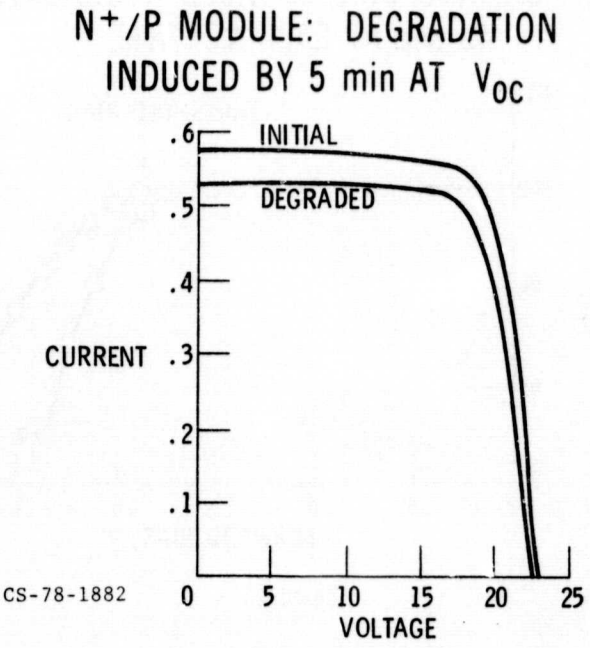

Figure 1.

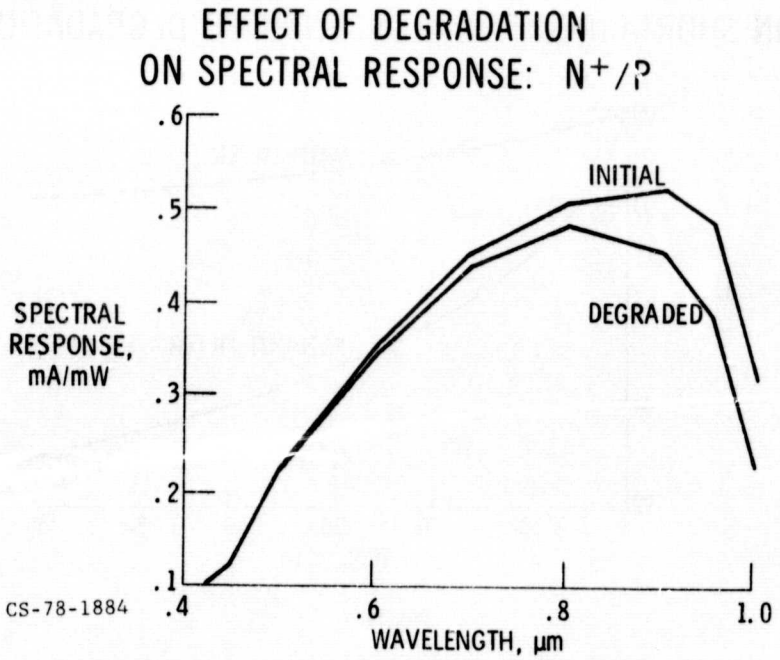

Figure 2.

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DARK FORWARD BIAS INDUCED DEGRADATION:
45 sec AT EACH VOLTAGE

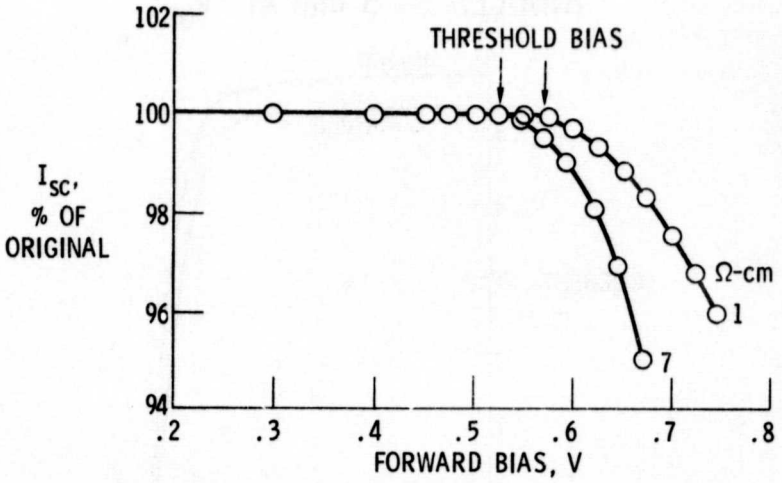

Figure 3.

EFFECT OF FILTERED (5 cm H_2O) TUNGSTEN LIGHT
ON SHORT-CIRCUIT CURRENT INDUCED DEGRADATION

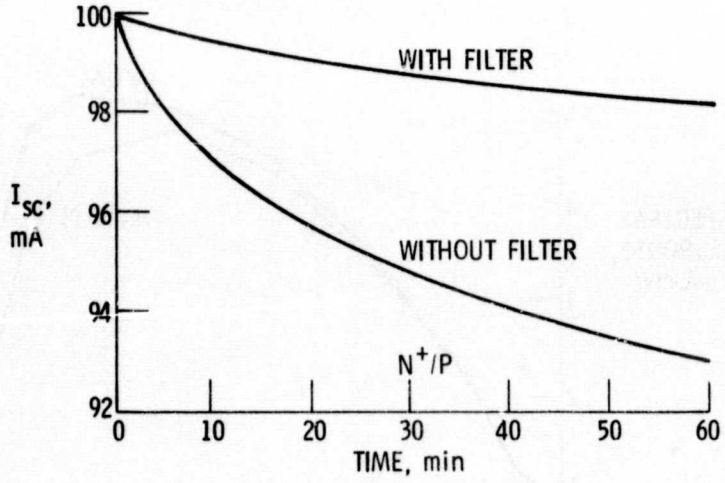

Figure 4.

EFFECT OF ENHANCEMENT
ON SPECTRAL RESPONSE: P^+/N

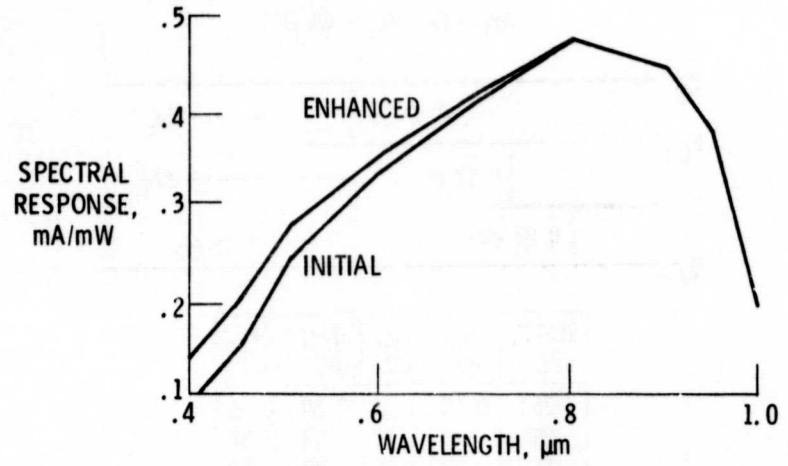

Figure 5.

CALCULATED EFFECT OF THIN LAYER OF SHORT DIFFUSION LENGTH MATERIAL ADJACENT TO DEPLETION REGION

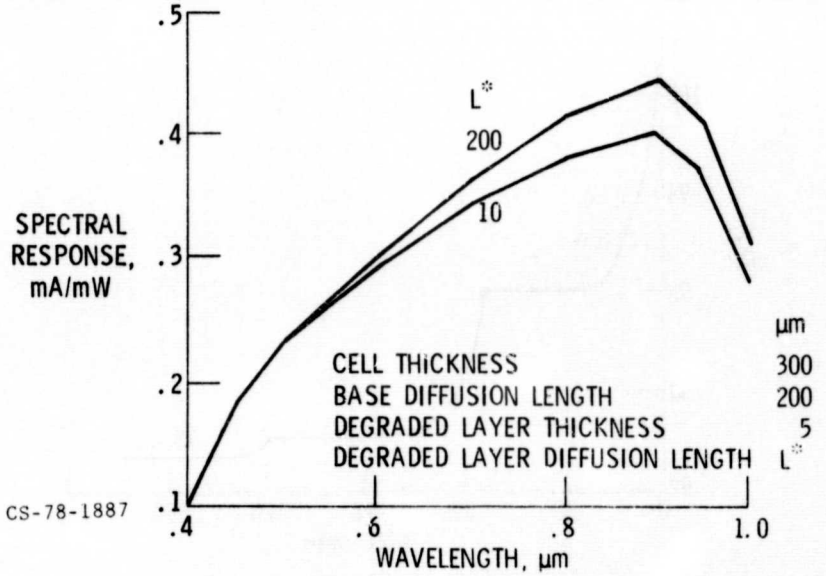

Figure 6.

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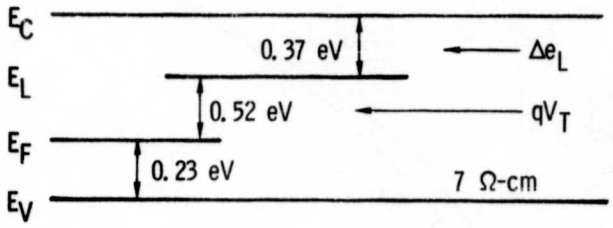
CALCULATED VALUES OF $\triangle e_L$ FROM DATA TAKEN AT VARIOUS TEMPERATURES

$\Delta e_L = E_G - (E_F + QV_T)$



TEMP, °C	E_F, eV	E_G, eV	qV_T, eV	Δe_L, eV
-25	0.18	1.14	0.60	0.36
25	.23	1.12	.52	.37
75	.28	1.10	.42	.40

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Figure 7.

EFFECT OF DARK FORWARD BIAS ON EXTENT OF DEGRADATION

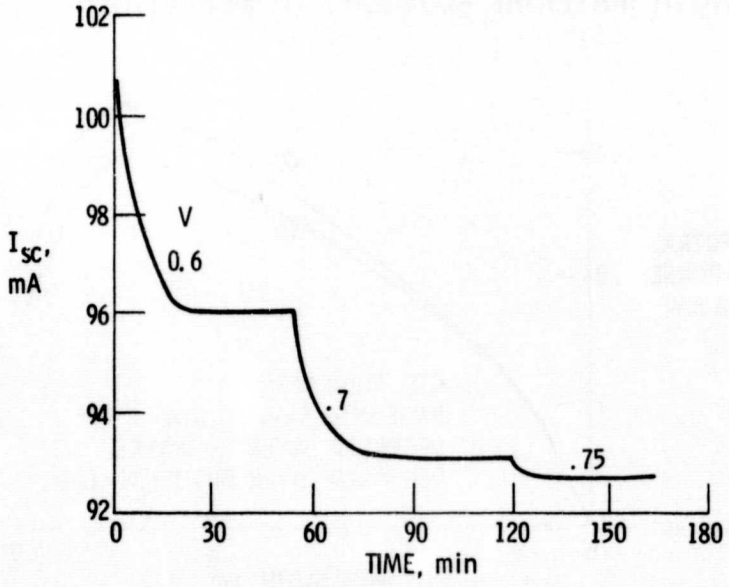

Figure 8.

EFFECTS OF CELL PROCESSING AND SURFACE TREATMENT ON EXTENT OF DEGRADATION IN N^+/P CELLS

DIFFUSION TEMP: 875^0 C

INITIAL MATERIAL	CELL PROCESSING	SURFACE CONDITION	PERCENT DEGRADATION*
TERRESTRIAL SOLAR CELL SILICON	GASEOUS DIFFUSION	DAMAGED	2.6
		POLISHED	0
	DOPED OXIDE DIFFUSION	DAMAGED	3.5
		POLISHED	0
10 OHM-CM CRUCIBLE GROWN SILICON	GASEOUS DIFFUSION	DAMAGED	0
		POLISHED	0
	DOPED OXIDE DIFFUSION	DAMAGED	1.3
		POLISHED	0
1 OHM-CM FLOAT ZONE SILICON	GASEOUS DIFFUSION	DAMAGED	2.1
		POLISHED	0
	DOPED OXIDE DIFFUSION	DAMAGED	8.7
		POLISHED	0

*5 MIN. V_{oc}, TUNGSTEN LIGHT, 100 MW/CM^2

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Figure 9.

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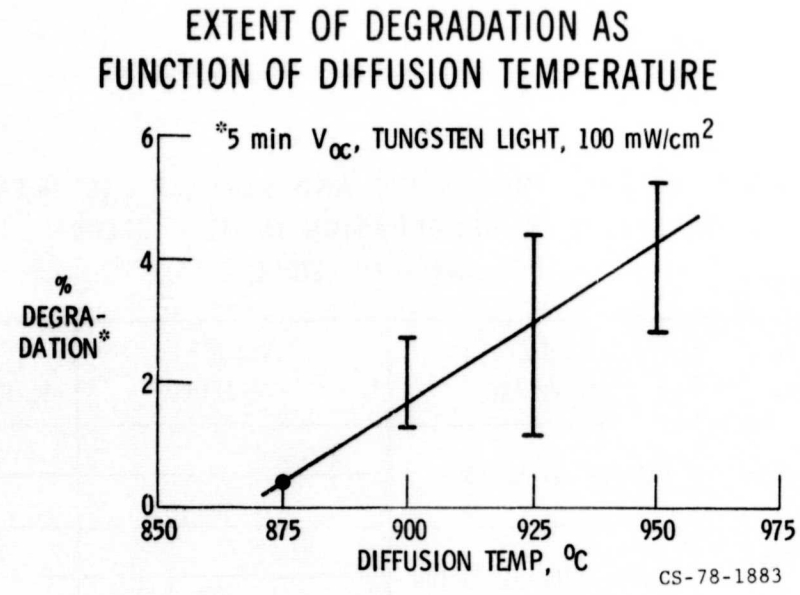

Figure 10.

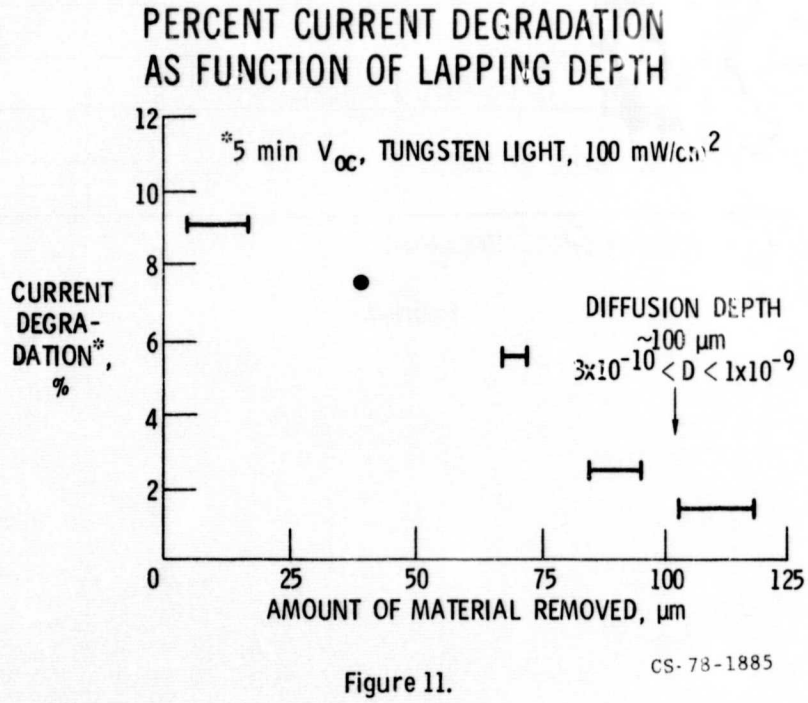

Figure 11.

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16. Abstract

An unexplained instability in terrestrial solar cell output under various use conditions has been observed. The effect is similar to but not identical with previously observed photon-induced degradation phenomenon in radiation damaged space solar cells. Reduction in cell output is observed in N^+/P cells upon exposure to illumination or upon the application of a sufficiently high forward bias. Conversely, an enhancement in output is observed when P^+/N cells are illuminated. Investigations performed on N^+/P cells indicates that a recombination center located at E_c - 0.37 eV in the forbidden band is responsible for the loss in output. The center is electrically inactive in its ground state but can be activated either by raising the minority carries quasi-Fermi level sufficiently close to the latest center energy level in the based gap, or by direct excitation of electrons from the valence band to the latent center level. The center has been identified as a complex of a lattice defect and a silver atom or cluster of atoms. The effect can be prevented either by preventing the introduction of silver or by eliminating lattice damage through sufficient surface material umoval prior to diffusion while at the same time restricting diffusion temperatures to 875° C or less. The effect in N-base cells is not fully understood at the present. It appears, however, that is either type of cell it is the P material that is responsible for the observed instabilities.

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